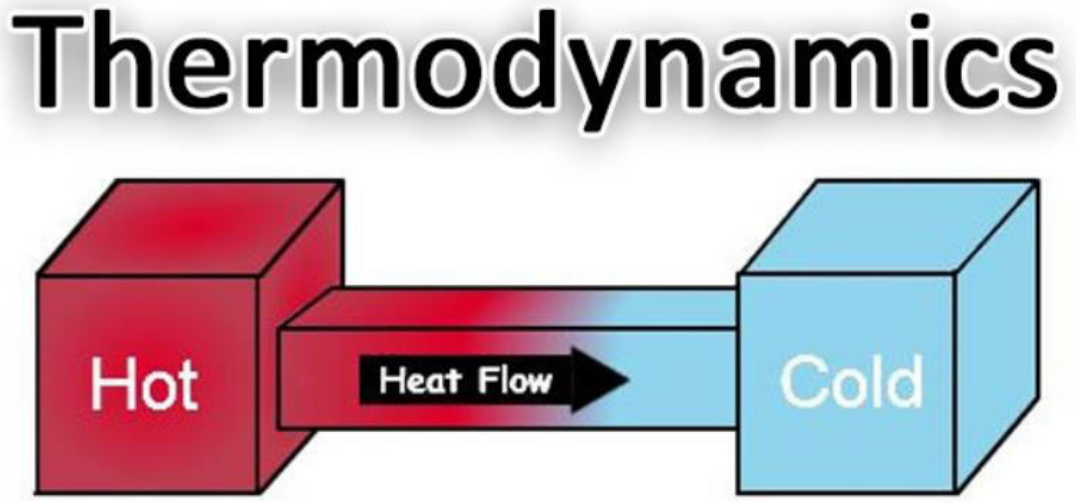
DEPARTMENT OF MECHANICAL ENGINEERING

ABIT

ENGINEERING THERMODYNAMICS



MODULE-II

PART-I

Availability and Irreversibility

AVAILABLE AND UNAVAILABLE ENERGY

- There are many forms in which an energy can exist. But even under ideal conditions all these forms cannot be converted completely into work. This indicates that energy has two parts :

  — Available part.

  — Unavailable part.

- 'Available energy' is the maximum portion of energy which could be converted into useful work by ideal processes which reduce the system to a dead state (a state in equilibrium with the earth and its atmosphere). Because there can be only one value for maximum work which the system alone could do while descending to its dead state, it follows immediately that 'Available energy' is a property.

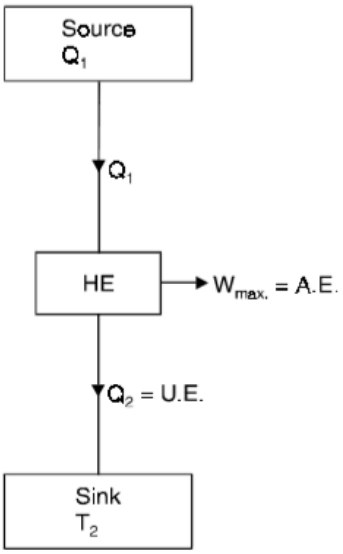
- A system which has a pressure difference from that of surroundings, work can be obtained from an expansion process, and if the system has a different temperature, heat can be transferred to a cycle and work can be obtained. But when the temperature and pressure becomes equal to that of the earth, transfer of energy ceases, and although the system contains internal energy, this energy is unavailable.

- Summarily available energy denote, the latent capability of energy to do work, and in this sense it can be applied to energy in the system or in the surroundings.

- The theoretical maximum amount of work which can be obtained from a system at any state p1 and T1 when operating with a reservoir at the constant pressure and temperature p0 and T0 is called 'availability'.

AVAILABLE ENERGY REFERRED TO A CYCLE

- The available energy (A.E.) or the available part of the energy supplied is the maximum work output obtainable from a certain heat input in a cyclic heat engine. The minimum energy that has to be rejected to the sink by the second law is called the unavailable energy (U.E.), or the unavailable part of the energy supplied.



- ∴ Q_1 = A.E. + U.E.
- or W_{max} = A.E. = Q_1 – U.E.

For the given values of the source temperature T1 and sink temperature T2, the reversible efficiency,

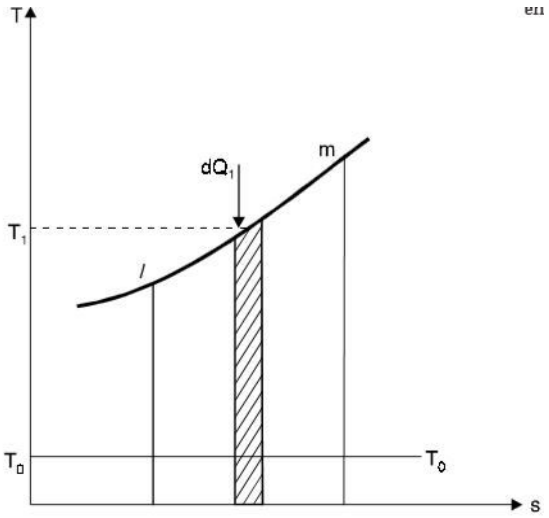
$$\eta_{rev} = 1 - \frac{T_2}{T_1}$$

For a given T_1, ηrev. will increase with the decrease of T_2. The lowest practicable temperature of heat rejection is the temperature of the surroundings, T_0.

$$\eta_{max} = 1 - \frac{T_0}{T_1} \; and \; W_{max} = (1 - \frac{T_0}{T_1})Q_1$$

Consider a finite process l-m, in which heat is supplied reversibly to a heat engine. Taking an elementary cycle, if dQ_1 is the heat received by the engine reversibly at T_1,

$$Then \; dW_{max} = \frac{T_1 - T_0}{T_1} dQ_1 = dQ_1 - \frac{T_0}{T_1} dQ_1 = A.E.$$

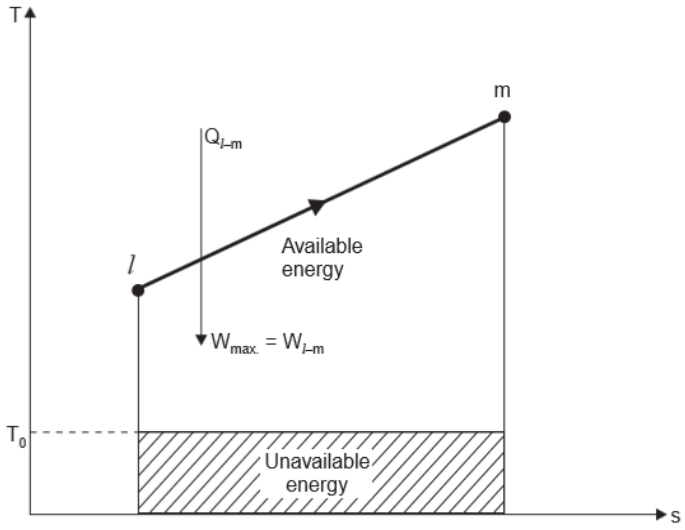


For the heat engine receiving heat for the whole process l-m, and rejecting heat at T_0

$$\int_l^m dW_{\max} = \int_l^m dQ_1 - \int_l^m \frac{T_0}{T_1} dQ_1$$

$$\therefore W_{\max} = A.E. = Q_{l-m} - T_0(S_l - S_m)$$

or unavailable energy, $U.E. = Q_{l-m} - W_{\max} \Rightarrow U.E. = T_0(S_l - S_m)$



Thus unavailable energy is the product of the lowest temperature of heat rejection, and the change of entropy of the system during the process of supplying heat.

DECREASE IN AVAILABLE ENERGY WHEN HEAT IS TRANSFERRED THROUGH A FINITE TEMPERATURE DIFFERENCE

When transfer of heat takes place through a finite temperature difference, there is a decrease in the availability of energy so transferred. Consider a reversible heat engine operating between temperatures T_1 and T_0 . Then

$Q_1 = T.\ \Delta s$;

$Q_2 = T_0\ \Delta s$;

and W = A.E. = $[T_1 - T_0]\ \Delta s$.

Assume that heat Q_1 is transferred through a finite temperature difference from the reservoir or source at T_1 to the engine absorbing heat at T_1', lower than T_1. The availability of Q_1 as received by the engine at T_1' can be found by allowing the engine to operate reversibly in a cycle between T_1' and T_0 receiving Q_1 and rejecting Q_2'.

Now, $Q_1 = T_1\Delta s = T_1'\Delta s'$

$T_1 > T_1'$

$$\therefore \Delta s' > \Delta s$$

$$Q_2 = T_0 \Delta s$$

$$Q_2' = T_0 \Delta s^1$$

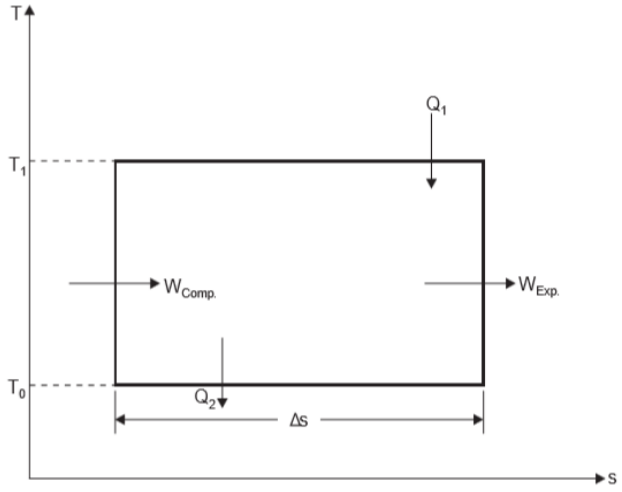
$$\because \Delta s' > \Delta s$$

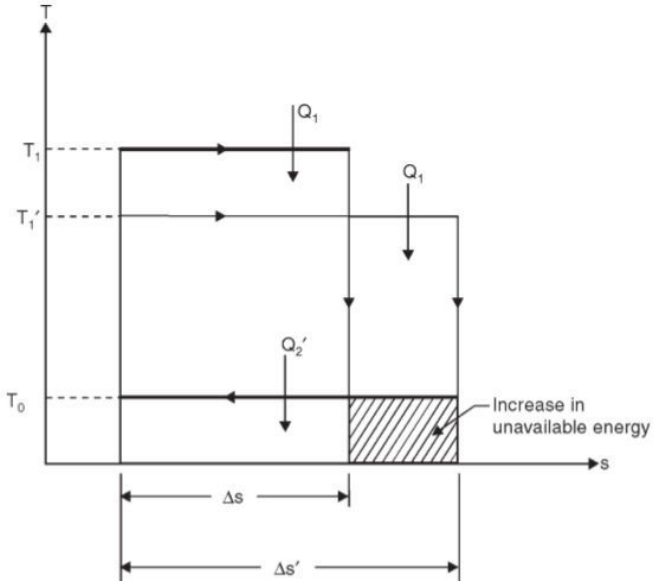
$$\therefore Q_2' > Q_2$$

$$\therefore W' = Q_1 - Q_2' = T_1' \Delta s' - T_0 \Delta s'$$

$$and W = Q_1 - Q_2 = T_1 \Delta s - T_0 \Delta S$$

$$\therefore W' < W, because Q_2' > Q_2$$





The loss of available energy due to irreversible heat transfer through finite temperature difference between the source and the working fluid during the heat addition process is given as :

$$W - W' = Q_2' - Q_2 = T_0 (\Delta s' - \Delta s)$$

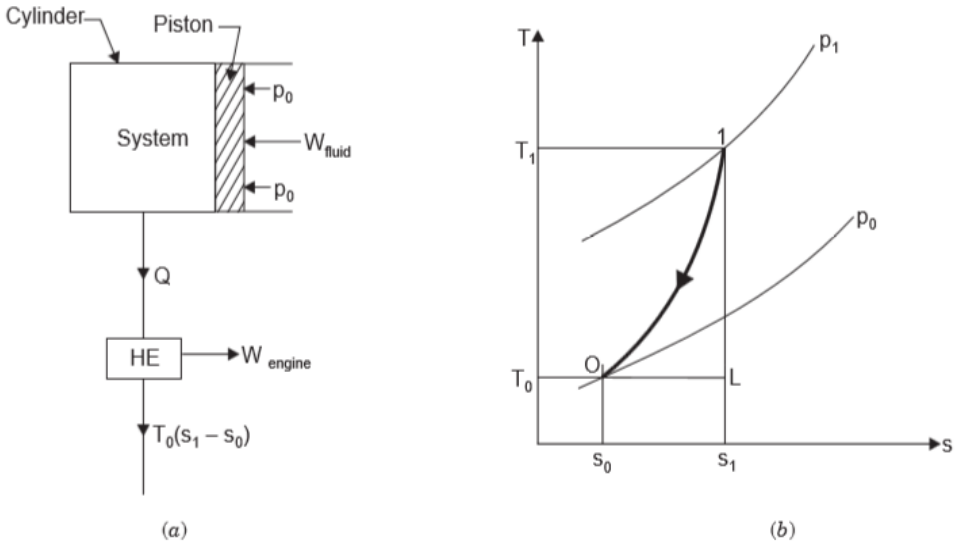
i.e., Decrease in available energy, A.E. = $T_0 (\Delta s' - \Delta s)$

Thus the decrease in A.E. is the product of the lowest feasible temperature of heat rejection and the additional entropy change in the system while receiving heat irreversibly, compared to the case of reversible heat transfer from the same source. The greater is the temperature difference ($T_1 - T_1'$), the greater is the heat rejection Q_2' and the greater will be the unavailable part of the energy supplied.

Energy is said to be degraded each time it flows through a finite temperature difference. That is, why the second law of thermodynamics is sometimes called the law of the degradation of energy, and energy is said to 'run down hill'.

AVAILABILITY IN NON-FLOW SYSTEMS

Let us consider a system consisting of a fluid in a cylinder behind a piston, the fluid expanding reversibly from initial condition of p_1 and T_1 to final atmospheric conditions of p_0 and T_0. Imagine also that the system works in conjunction with a reversible heat engine which receives heat reversibly from the fluid in the cylinder such that the working substance of the heat engine follows the cycle O1LO as shown in Fig. , where $s_1 = s_L$ and $T_0 = T_L$ (the only possible way in which this could occur would be if an infinite number of reversible heat engines were arranged in parallel, each operating on a Carnot cycle, each one receiving heat at a different constant temperature and each one rejecting heat at T_0). The work done by the engine is given by :



W_{engine} = Heat supplied – Heat rejected = $Q - T_0 (s_1 - s_0)$……..(i)

The heat supplied to the engine is equal to the heat rejected by the fluid in the cylinder. Therefore, for the fluid in the cylinder undergoing the process 1 to 0, we have

$$-Q = (u_0 - u_1) + W_{fluid}$$

i.e., $W_{fluid} = (u_1 - u_0) - Q$……(ii)

Adding eqns. (i) and (ii), we get

$$W_{fluid} + W_{engine} = [(u_1 - u_0) - Q] + [Q - T_0 (s_1 - s_0)]$$

$$= (u_1 - u_0) - T_0 (s_1 - s_0)$$

The work done by the fluid on the piston is less than the total work done by the fluid, since there is no work done on the atmosphere which is at constant pressure p_0

i.e., Work done on atmosphere = $p_0 (v_0 – v_1)$

Hence, maximum work available = $(u_1 – u_0) – T_0 (s_1 – s_0) – p_0 (v_0 – v_1)$

Note. When a fluid undergoes a complete cycle then the net work done on the atmosphere is zero.

$W_{max} = (u_1 + p_0v_1 – T_0s_1) – (u_0 + p_0v_0 – T_0s_0)$

$\therefore W_{max} = a_1 – a_0$

The property, $a = u + p_0v – T_0s$ (per unit mass) is called the non-flow availability function.

AVAILABILITY IN STEADY FLOW SYSTEMS

Consider a fluid flowing steadily with a velocity C_1 from a reservoir in which the pressure and temperature remain constant at p_1 and T_1 through an apparatus to atmospheric pressure of p_0. Let the reservoir be at a height Z_1 from the datum, which can be taken at exit from the apparatus, i.e., $Z_0 = 0$. For maximum work to be obtained from the apparatus the exit velocity, C_0, must be zero. It can be shown that a reversible heat engine working between the limits would reject $T_0 (s_1 – s_0)$ units of heat, where T_0 is the atmospheric temperature. Thus, we have

$$W_{max} = (h_1 + \frac{C_1^2}{2} + Z_1 g) – h_0 – T_0 (s_1 – s_0)$$

In several thermodynamic systems the kinetic and potential energy terms are negligible

i.e., $W_{max} = (h_1 – T_0s_1) – (h_0 – T_0s_0)$

$= b – b_0$

The property, $b = h – T_0s$ (per unit mass) is called the steady-flow availability function.

[In the equation $b = h – T_0s$; the function ‘b’ (like the function ‘a’) is a composite property of a system and its environment ; this is also known as Keenan function].

Note 1. The alternative names for availability and unavailable quantity $T_0\Delta s$ are energy and aenergy respectively.

2. The only difference between $a = u + p_0v – T_0s$ function and $b = (h – T_0s) = (u + pv – T_0s)$ function is in pressure only.

HELMHOLTZ AND GIBBS FUNCTIONS

The work done in a non-flow reversible system (per unit mass) is given by :

$W = Q – (u_0 – u_1) = T.ds – (u_0 – u_1)$

$= T (s_0 – s_1) – (u_0 – u_1)$

i.e., $W = (u_1 – Ts_1) – (u_0 – Ts_0)$

The term (u – Ts) is known as Helmholtz function. This gives maximum possible output when the heat Q is transferred at constant temperature and is the case with a very large source.

If work against atmosphere is equal to $p_0 (v_0 – v_1)$, then the maximum work available,

W_{max} = W – work against atmosphere

$= W – p_0 (v_0 – v_1)$

$= (u_1 – Ts_1) – (u_0 – Ts_0) – p_0 (v_0 – v_1)$

$= (u_1 + p_0v_1 – Ts_1) – (u_0 + p_0v_0 – Ts_0)$

$= (h_1 – Ts_1) – (h_0 – Ts_0)$

i.e., $W_{max} = g_1 – g_0$

where g = h – T.s is known as Gibb's function or free energy function.

The maximum possible available work when system changes from 1 to 2 is given by

$W_{max} = (g_1 – g_0) – (g_2 – g_0) = g_1 – g_2$

Similarly, for steady flow system the maximum work available is given by

$W_{max} = (g_1 – g_2) + (KE_1 – KE_2) + (PE_1 – PE_2)$

where K.E. and P.E. represent the kinetic and potential energies.

It may be noted that Gibb's function g = (h – Ts) is a property of the system where availability function $a = (u + p_0v – T_0s)$ is a composite property of the system and surroundings.

Again, $a = u + p_0v – T_0s$

$b = u + pv – T_0s$

$g = u + pv – Ts$

When state 1 proceeds to dead state (zero state) a = b = g.

IRREVERSIBILITY

The actual work which a system does is always less than the idealized reversible work, and the difference between the two is called the irreversibility of the process.

Thus, Irreversibility, $I = W_{max} – W$

This is also sometimes referred to as 'degradation' or 'dissipation'. For a non-flow process between the equilibrium states, when the system exchanges heat only with environment, irreversibility (per unit mass),

$i = [(u_1 - u_2) - T_0(s_1 - s_2)] - [(u_1 - u_2) + Q]$

$= T_0 (s_2 - s_1) - Q$

$= T_0 (\Delta s)_{system} + T_0 (\Delta s)_{surr.}$

i.e., $i = T_0 [(\Delta s)_{system} + (\Delta s)_{surr.}]$

$\therefore i \geq 0$

Similarly, for steady flow-process

$i = W_{max} - W$ (per unit mass)

$$= [(b_1 + \frac{C_1^2}{2} + gZ_1) - (b_2 + \frac{C_2^2}{2} + gZ_2)] - [(h_1 + \frac{C_1^2}{2} + gZ_1) - (h_2 + \frac{C_2^2}{2} + gZ_2) + Q]$$

$= T_0 (s_2 - s_1) - Q$

$= T_0 (\Delta s)_{system} + T_0 (\Delta s)_{surr.}$

i.e., $i = T_0 (\Delta s_{system} + \Delta s_{surr.})$

The same expression for irreversibility applies to both flow and non-flow processes.

The quantity $T_0 (\Delta s_{system} + \Delta s_{surr.})$ represents (per unit mass) an increase in unavailable energy (or energy).

EFFECTIVENESS

Effectiveness is defined as the ratio of actual useful work to the maximum useful work. The useful output of a system is given by the increase of availability of the surroundings.

$$Effectiveness, \varepsilon = \frac{Increase in availability of surroundings}{loss of availability of system}$$

For a compression or heating process the effectiveness is given by

$$Effectiveness, \varepsilon = \frac{Increase in availability of system}{loss of availability of surroundings} = \frac{W_{useful}}{W_{max.useful}}$$

The effectiveness of an actual process is always less than unity. Thus effectiveness of a process is the measure of the extent to which advantage has been taken of an opportunity to obtain useful work.

Example . One kg of air is compressed polytropically from 1 bar pressure and temperature of 300 K to a pressure of 6.8 bar and temperature of 370 K. Determine the irreversibility if the sink temperature is 293 K. Assume R = 0.287 kJ/kg K, c_p = 1.004 kJ/kg K and c_v = 0.716 kJ/kg K.

Solution. Irreversibility I = $W_{max} - W_{act}$

$-W_{max}$ = Change in internal energy – T_0 × Change in entropy

or $-W_{max} = (u_2 - u_1) - T_0(s_2 - s_1) = W_{rev}$

or $-W_{max} = c_v(T_2 - T_1) - T_0[c_p \ln (T_2/T_1) - R \ln (p_2/p_1)]$

$= 0.716(370 - 300) - 293 \times [1.005 \ln (370/300) - 0.287 \ln (6.8/1)]$

$W_{max} = -149.53$ kJ/kg = W_{rev}

(negative sign indicates that work is done on air)

The index of compression 'n' is given by

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{[(n-1)/n)]} \Rightarrow \frac{n-1}{n} = \frac{\ln(T_2/T_1)}{\ln(P_2/P_1)} = \frac{\ln(370/300)}{\ln(6.8/1)} \Rightarrow n = 1.123$$

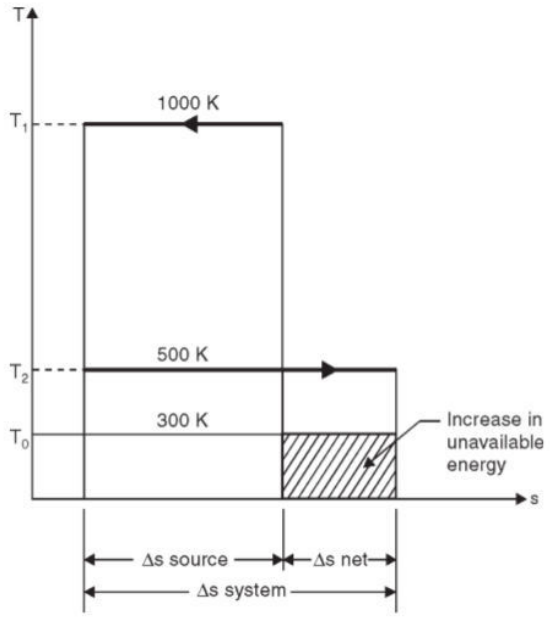
$$W_{actual} = \frac{mR(T_1 - T_2)}{n-1} = \frac{1X0.287(300-370)}{1.123-1} = -163.33kJ/kg$$

I = $W_{rev} - W_{act}$ = – 149.53 – (– 163.33) = 13.8 kJ/kg. (Ans.)

Example. A system at 500 K receives 7200 kJ/min from a source at 1000 K. The temperature of atmosphere is 300 K. Assuming that the temperatures of system and source remain constant during heat transfer find out :

(i) The entropy produced during heat transfer ;

(ii) The decrease in available energy after heat transfer.



Temperature of source, T_1 = 1000 K

Temperature of system, T_2 = 500 K

Temperature of atmosphere, T_0 = 300 K

Heat received by the system, Q = 7200 kJ/min.

(i) Net change of entropy :

Change in entropy of the source during heat transfer

$$= \frac{-Q}{T_1} = \frac{-7200}{1000} = -7.2 kJ/\min\ K$$

Change in entropy of the system during heat transfer

$$= \frac{Q}{T_2} = \frac{7200}{500} = 14.4 kJ/\min\ K$$

The net change of entropy, ΔS = – 7.2 + 14.4 = 7.2 kJ/min-K. (Ans.)

(ii) Decrease in available energy :

Available energy with source = (1000 – 300) × 7.2 = 5040 kJ

Available energy with the system = (500 – 300) × 14.4 = 2880 kJ

∴ Decrease in available energy = 5040 – 2880 = 2160 kJ. (Ans.)

[Also,increase in available energy

$$= T_0(S_2 - S_1) = T_0\Delta S = 300X7.2 = 2160kJ$$

Example. 8 kg of air at 650 K and 5.5 bar pressure is enclosed in a closed system. If the atmosphere temperature and pressure are 300 K and 1 bar respectively, determine :

(i) The availability if the system goes through the ideal work producing process.

(ii) The availability and effectiveness if the air is cooled at constant pressure to atmospheric temperature without bringing it to complete dead state. Take c_v = 0.718 kJ/kg K ; c_p= 1.005 kJ/kg K.

Solution. Mass of air, m = 8 kg

Temperature, T_1 = 650 K

Pressure, p_1 = 5.5 bar

Atmospheric pressure, p_0 = 1 bar

Atmospheric temperature, T_0 = 300 K

For air : c_v = 0.718 kJ/kg K ; c_p = 1.005 kJ/kg K.

(i) Change in available energy (for bringing the system to dead state),

= m[(u_1 – u_0) – $T_0\Delta s$]

Also, $$\Delta s = c_v \log_e\left(\frac{T_1}{T_0}\right) + R\log_e\left(\frac{v_1}{v_0}\right)$$

Using the ideal gas equation,

$$\frac{p_1v_1}{T_1} = \frac{p_0v_0}{T_0} \Rightarrow \frac{v_0}{v_1} = \frac{p_1}{p_0}.\frac{T_0}{T_1} = \frac{5.5}{1}.\frac{300}{650} = 2.54$$

$$\therefore \Delta s = 0.718\log_e\left(\frac{650}{300}\right) + 0.287\log_e\left(\frac{1}{2.54}\right)$$

= 0.555 + (– 0.267) = 0.288 kJ/kg K

∴ Change in available energy

= m[(u1 – u0) – T0Δs] = m[cv(T1 – T0) – T0Δs]

= 8[0.718(650 – 300) – 300 × 0.288] = 1319.2 kJ

Loss of availability per unit mass during the process = p0 (v0 – v1) per unit mass

Total loss of availability = p0(V0 – V1)

But, $V_1 = mRT_1 / P_1 = \frac{8X287X650}{5.5X10^5} = 2.713m^3$

and V0 = 2.54 × 2.713 = 6.891 m^3

∴ Loss of availability =(1x10^5/10^3) × (6.891 – 2.713) = 417.8 kJ. (Ans.)

(ii) Heat transferred during cooling (constant pressure) process = m. cp (T1 – T0) = 8 × 1.005 (650 – 300) = 2814 kJ

Change in entropy during cooling

$$\Delta s = mc_p \log_e\left(\frac{T_1}{T_0}\right) = 8X1.005X \log_e\left(\frac{650}{300}\right) = 6.216kJ/K$$

Unavailable energy = T0 ΔS = 300 × 6.216 = 1864.8 Kj

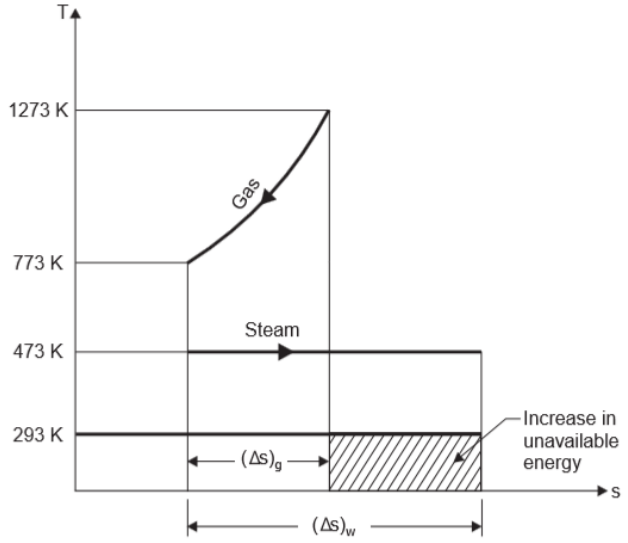
Available energy = 2814 – 1864.8 = 949.2 kJ. (Ans.)

$$Effecetiveness, \varepsilon = \frac{Availableenergy}{Changeinavailableenergy} = \frac{949.2}{1319.2} = 0.719$$

Example. In a power station, the saturated steam is generated at 200ºC by transferring the heat from hot gases in a steam boiler. Find the increase in total entropy of the combined system of gas and water and increase in unavailable energy due to irreversible heat transfer. The gases are cooled from 1000°C to 500°C and all the heat from gases goes to water. Assume water enters the boiler at saturated condition and leaves as saturated steam.

Take : c_{pg} (for gas) = 1.0 kJ/kg K, h_{fg} (latent heat of steam at 200°C) = 1940.7 kJ/kg. Atmospheric temperature = 20°C. Obtain the results on the basis of 1 kg of water.

Solution. Refer Fig.. Temperature of saturation steam = 200 + 273 = 473 K



Initial temperature of gases = 1000 + 273 = 1273 K

Final temperature of gases = 500 + 273 = 773 K

For gases : c_{pg} = 1 kJ/kg K

Latent heat of steam of 200°C

saturation temperature, h_{fg} = 1940.7 kJ/kg

Atmospheric temperature = 20 + 273 = 293 K

Heat lost by gases = Heat gained by 1 kg saturated water when it is converted to steam at

200°C.

∴ $m_g c_{pg}$ (1273 – 773) = 1940.7 [where m_g = mass of gases, c_{pg} = specific heat of gas at constant pressure]

$$m_g = \frac{1940.7}{1.0X(1273-773)} = 3.88kg$$

Change of entropy of mg kg of gas,

$$(\Delta S)_g = m_g c_{pg} \log_e\left(\frac{773}{1273}\right) = 3.88X1.0\log_e\left(\frac{773}{1273}\right) = -1.935kJ/K$$

Change of entropy of water (per kg) when it is converted into steam,

$$(\Delta s)_w = \frac{h_{fg}}{T_s} = \frac{1940.7}{(200+273)} = 4.103 kJ/kgK$$

Net change in entropy due to heat transfer = – 1.935 + 4.103 = 2.168 kJ/K. (Ans.)

Increase in unavailable energy due to heat transfer

= 293 × 2.168,

i.e., cross hatched area = 635.22 kJ per kg of steam formed. (Ans.)

PART-II

General Thermodynamic property relations

FUNDAMENTALS OF PARTIAL DIFFERENTIATION

- Let three variables are represented by x, y and z. Their functional relationship may be expressed in the following forms :

  f(x, y, z) = 0 ...(i)

  x = x(y, z) ...(ii)

  y = y(x, z) ...(iii)

  z = z(x, y) ...(iv)

  Let x is a function of two independent variables y and z

  x = x(y, z)

Then the differential of the dependent variable x is given by

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

where dx is called an exact differential.

If $\left(\frac{\partial x}{\partial y}\right)_z = M$ and $\left(\frac{\partial x}{\partial z}\right)_y = N$

Then dx = Mdy + Ndz

Partial differentiation of M and N with respect to z and y, respectively, gives

$$\frac{\partial M}{\partial z} = \frac{\partial^2 x}{\partial y \partial z} \quad \text{and} \quad \frac{\partial N}{\partial y} = \frac{\partial^2 x}{\partial z \partial y}$$

Or, $$\frac{\partial M}{\partial z} = \frac{\partial N}{\partial y}$$

dx is a perfect differential when above eqn. is satisfied for any function x.

Similarly if y = y(x, z) and z = z(x, y)

then from these two relations, we have

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x \left[\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy\right]$$

$$= \left[\left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y\right] dx + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$= \left[\left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y\right] dx + dy$$

Or, $$\left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = 0 \Rightarrow \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial y}{\partial x}\right)_z$$

Or, $$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$

In terms of p, v and T, the following relation holds good

$$\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial v}{\partial T}\right)_p = -1$$

SOME GENERAL THERMODYNAMIC RELATIONS

The first law applied to a closed system undergoing a reversible process states that

dQ = du + pdv

According to second law,

$$ds = \left(\frac{dQ}{T}\right)_{rev.}$$

Combining these equations, we get

Tds = du + pdv

or du = Tds – pdv

The properties h, f and g may also be put in terms of T, s, p and v as follows :

dh = du + pdv + vdp = Tds + vdp

Helmholtz free energy function,

df = du – Tds – sdT

= – pdv – sdT

Gibb's free energy function,

dg = dh – Tds – sdT = vdp – sdT

Each of these equations is a result of the two laws of thermodynamics.

Since du, dh, df and dg are the exact differentials, we can express them as

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv,$$

$$dh = \left(\frac{\partial h}{\partial s}\right)_p ds + \left(\frac{\partial h}{\partial p}\right)_s dp,$$

$$df = \left(\frac{\partial f}{\partial v}\right)_T dv + \left(\frac{\partial f}{\partial T}\right)_v dT,$$

$$dg = \left(\frac{\partial g}{\partial p}\right)_T dp + \left(\frac{\partial g}{\partial T}\right)_p dT.$$

Comparing these equations with previous equations we may equate the corresponding co-efficients. For example, from the two equations for du, we have

$$\left(\frac{\partial u}{\partial s}\right)_v = T \quad \text{and} \quad \left(\frac{\partial u}{\partial v}\right)_s = -p$$

The complete group of such relations may be summarised as follows :

$$\left(\frac{\partial u}{\partial s}\right)_v = T = \left(\frac{\partial h}{\partial s}\right)_p$$

$$\left(\frac{\partial u}{\partial v}\right)_s = -p = \left(\frac{\partial f}{\partial v}\right)_T$$

$$\left(\frac{\partial h}{\partial p}\right)_s = v = \left(\frac{\partial g}{\partial p}\right)_T$$

$$\left(\frac{\partial f}{\partial T}\right)_v = -s = \left(\frac{\partial g}{\partial T}\right)_p$$

Also, $$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$$

These equations are known as Maxwell relations.

ENTROPY EQUATIONS (Tds Equations)

- Since entropy may be expressed as a function of any other two properties, e.g. temperature T and specific volume v,

  s = f(T, v)

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

Or, $$Tds = T\left(\frac{\partial s}{\partial T}\right)_v dT + T\left(\frac{\partial s}{\partial v}\right)_T dv$$

But for a reversible constant volume change

$$dq = c_v (dT)_v = T(ds)_v) \Rightarrow c_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

But, $\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$

So, we get,

$$Tds = c_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dv$$

This is known as the first form of entropy equation or the first Tds equation.

Similarly, writing

s = f(T, p)

$$Tds = T\left(\frac{\partial s}{\partial T}\right)_p dT + T\left(\frac{\partial s}{\partial p}\right)_T dp$$

Where, $c_p = T\left(\frac{\partial s}{\partial T}\right)_p$

Also, $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$

Hence,

$$Tds = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$$

This is known as the second form of entropy equation or the second Tds equation.

EQUATIONS FOR INTERNAL ENERGY AND ENTHALPY

(i) Let u = f(T, v)

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv = c_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

To evaluate, $\left(\frac{\partial u}{\partial v}\right)_T$ let u = f (s, v)

Then, $du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$

Or, $\left(\frac{\partial u}{\partial v}\right)_T = \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial v}\right)_T + \left(\frac{\partial u}{\partial v}\right)_s$

But, $\left(\frac{\partial u}{\partial s}\right)_v = T, \quad \left(\frac{\partial s}{\partial v}\right)_t = \left(\frac{\partial s}{\partial T}\right)_v \; and \left(\frac{\partial u}{\partial v}\right)_s = -p$

Hence, $\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$

This is sometimes called the energy equation.

$$du = c_v dT + \left\{T\left(\frac{\partial p}{\partial T}\right)_v - p\right\} dv$$

(ii) To evaluate dh we can follow similar steps as under

h = f(T, p)

$$dh = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp = c_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp$$

To find, $\left(\frac{\partial h}{\partial p}\right)_T$, let h = f(s, p)

Then, $dh = \left(\frac{\partial h}{\partial s}\right)_p ds + \left(\frac{\partial h}{\partial p}\right)_s dp$

$$\left(\frac{\partial h}{\partial p}\right)_T = \left(\frac{\partial h}{\partial s}\right)_p \left(\frac{\partial s}{\partial p}\right)_T + \left(\frac{\partial h}{\partial p}\right)_s$$

But, $\left(\frac{\partial h}{\partial s}\right)_p = T, \left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial p}\right)_p, \left(\frac{\partial h}{\partial p}\right)_s = v$

Hence, $\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$

So we get,

$$dh = c_p dT + \left\{ v - T\left(\frac{\partial v}{\partial T}\right)_p \right\} dp$$

MEASURABLE QUANTITIES

- Out of eight thermodynamic properties, as earlier stated, only p, v and T are directly measurable. Let us now examine the information that can be obtained from measurements of these primary properties, and then see what other easily measurable quantities can be introduced.
- The following will be discussed :

  (i) Equation of state

  (ii) Co-efficient of expansion and compressibility

  (iii) Specific heats

  (iv) Joule-Thomson co-efficient

Equation of State

- Let us imagine a series of experiments in which the volume of a substance is measured over a range of temperatures while the pressure is maintained constant, this being repeated for various pressures.
- The results might be represented graphically by a three-dimensional surface, or by a family of constant pressure lines on a v-T diagram. It is useful if an equation can be found to express the relation between p, v and T, and this can always be done over a limited range of states.
- No single equation will hold for all phases of a substance, and usually more than one equation is required even in one phase if the accuracy of the equation is to match that of the experimental results.
- Equations relating p, v and T are called equations of state or characteristic equations. Accurate equations of state are usually complicated, a typical form being

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + ...$$

where A, B, C, ... are functions of temperature which differ for different substances.

- An equation of state of a particular substance is an empirical result, and it cannot be deduced from the laws of thermodynamics. Nevertheless the general form of the equation may be predicted from hypotheses about the microscopic structure of matter. This type of prediction has been developed to a high degree of precision for gases, and to a lesser extent for liquids and solids.

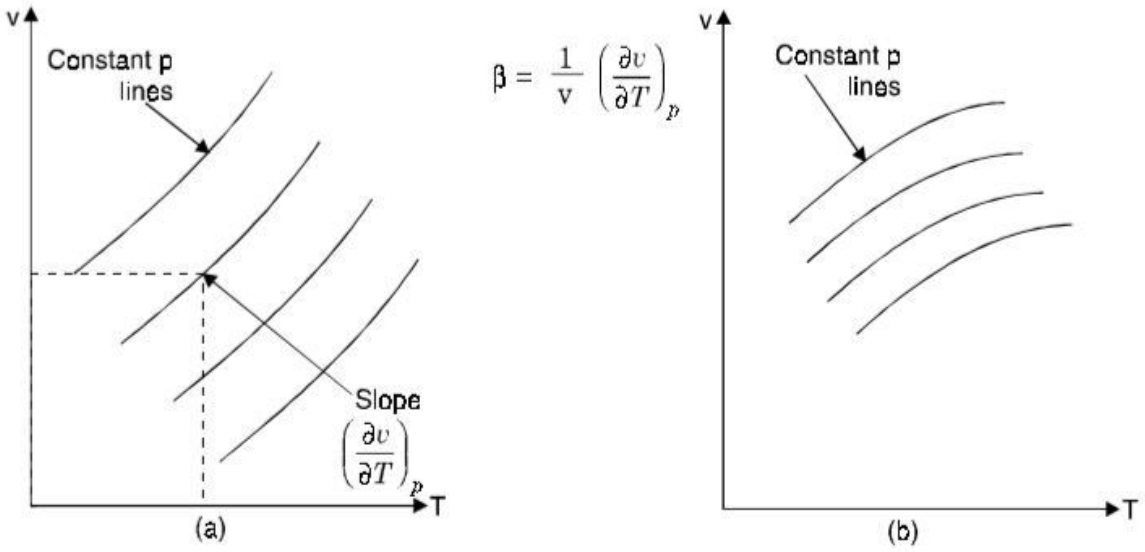
- The simplest postulates about the molecular structure of gases lead to the concept of the perfect gas which has the equation of state pv = RT. Experiments have shown that the behaviour of real gases at low pressure with high temperature agrees well with this equation.

Co-efficient of Expansion and Compressibility

- From p-v-T measurements, we find that an equation of state is not the only useful information which can be obtained. When the experimental results are plotted as a series of constant pressure lines on a v-T diagrams, as in Fig. (a), the slope of a constant pressure line at any given state is $\left(\frac{\partial v}{\partial T}\right)_p$.

- If the gradient is divided by the volume at that state, we have a value of a property of the substance called its co-efficient of cubical expansion β. That is,

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$



- Value of β can be tabulated for a range of pressures and temperatures, or plotted graphically as in Fig. (b).

- For solids and liquids over the normal working range of pressure and temperature, the variation of β is small and can often be neglected.

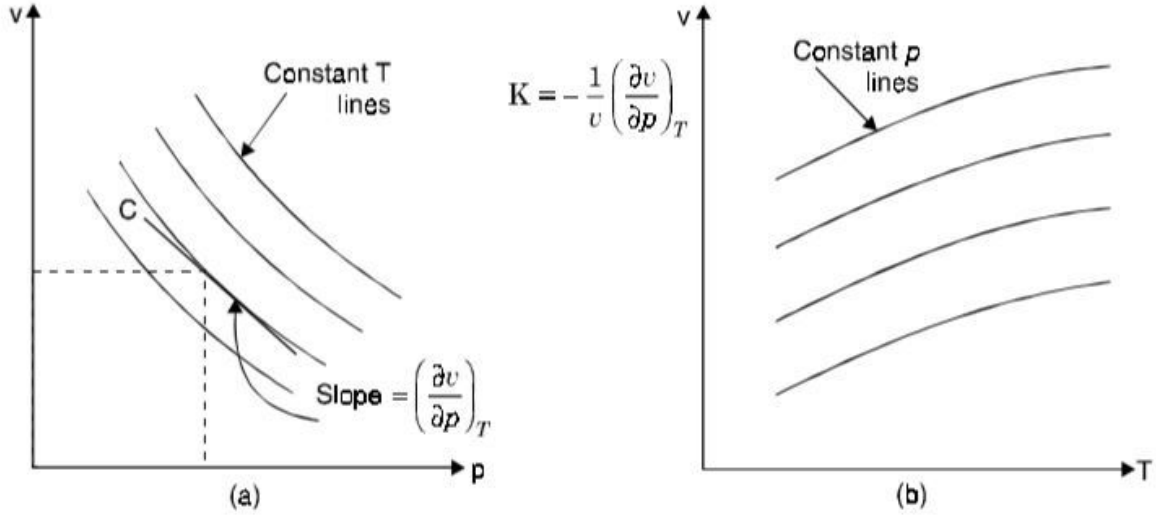
- In tables of physical properties β is usually quoted as an average value over a small range of temperature, the pressure being atmospheric. This average co-efficient may be symbolised by β and it is defined by

$$\beta = \frac{v_2 - v_1}{v_1(T_2 - T_1)}$$

- Fig. (a) can be replotted to show the variation of volume with pressure for various constant values of temperature. In this case, the gradient of a curve at any state is $\left(\frac{\partial v}{\partial p}\right)_T$.

- When this gradient is divided by the volume at that state, we have a property known as the compressibility K of the substance. Since this gradient is always negative, i.e., the volume of a substance always decreases with increase of pressure when the temperature is constant, the compressibility is usually made a positive quantity by defining it as

$$K = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$$



- K can be regarded as a constant for many purposes for solids and liquids. In tables of properties it is often quoted as an average a value over a small range of pressure at atmospheric temperature, i.e.,

$$\overline{K} = -\frac{v_2 - v_1}{v_1(p_2 - p_1)}$$

When β and K are known, we have

$$\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_p \left(\frac{\partial v}{\partial p}\right)_T = -1$$

Since, $\left(\frac{\partial v}{\partial T}\right)_p = \beta v$

And $\left(\frac{\partial v}{\partial p}\right)_T = -Kv,$

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{\beta}{K}$$

When the equation of state is known, the co-efficient of cubical expansion and compressibility can be found by differentiation. For a perfect gas, for example, we have

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{p}$$

And $\left(\frac{\partial v}{\partial p}\right)_T = \frac{RT}{p^2}$

Hence, $\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{pv} = \frac{1}{T}$

And $K = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{RT}{p^2 v} = \frac{1}{p}$

Specific Heats

- Following are the three differential co-efficients which can be relatively easily determined experimentally.
- Consider the first quantity $\left(\frac{\partial u}{\partial T}\right)_v$. During a process at constant volume, the first law informs us that an increase of internal energy is equal to heat supplied. If a calorimetric experiment is conducted with a known mass of substance at constant volume, the quantity of heat Q required to raise the temperature of unit mass by ΔT may be measured.
- We can then write : $\left(\frac{\Delta u}{\Delta T}\right)_v = \left(\frac{Q}{\Delta T}\right)_v$. The quantity obtained this way is known as the mean specific heat at constant volume over the temperature range ΔT.
- It is found to vary with the conditions of the experiment, i.e., with the temperature range and the specific volume of the substance.

- As the temperature range is reduced the value approaches that of $\left(\frac{\partial u}{\partial T}\right)_v$, and the true specific heat at constant volume is defined by $c_v = \left(\frac{\partial u}{\partial T}\right)_v$. This is a property of the substance and in general its value varies with the state of the substance, e.g., with temperature and pressure.
- According to first law of thermodynamics the heat supplied is equal to the increase of enthalpy during a reversible constant pressure process. Therefore, a calorimetric experiment carried out with a substance at constant pressure gives us, $\left(\frac{\Delta h}{\Delta T}\right)_p = \left(\frac{Q}{\Delta T}\right)_p$ which is the mean specific heat at constant pressure.
- As the range of temperature is made infinitesimally small, this becomes the rate of change of enthalpy with temperature at a particular state defined by T and p, and this is true specific heat at constant pressure defined by $c_p = \left(\frac{\partial h}{\partial T}\right)_p$. c_p also varies with the state, e.g., with pressure and temperature.
- The description of experimental methods of determining cp and cv can be found in texts on physics. When solids and liquids are considered, it is not easy to measure cv owing to the stresses set up when such a substance is prevented from expanding. However, a relation between cp, cv, β and K can be found as follows, from which cv may be obtained if the remaining three properties have been measured.
- The First Law of Thermodynamics, for a reversible process states that dQ = du + p dv
- Since we may write u = ϕ(T, v), we have

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$\therefore dQ = \left(\frac{\partial u}{\partial T}\right)_v dT + \left\{p + \left(\frac{\partial u}{\partial v}\right)_T\right\} dv = c_v dT + \left\{p + \left(\frac{\partial u}{\partial v}\right)_T\right\} dv$$

This is true for any reversible process, and so, for a reversible constant pressure process,

$$dQ = c_p (dT)_p = c_v dT + \left\{ p + \left(\frac{\partial u}{\partial v} \right)_T \right\} (dv)_p$$

$$\Rightarrow c_p - c_v = \left\{ p + \left(\frac{\partial u}{\partial v} \right)_T \right\} \left(\frac{\partial v}{\partial T} \right)_p$$

$$also \left(\frac{\partial p}{\partial T} \right)_v = \left(\frac{\partial s}{\partial v} \right)_T = \frac{1}{T} \left\{ p + \left(\frac{\partial u}{\partial v} \right)_T \right\}, and therefore$$

$$c_p - c_v = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_v$$

$$Now, we have$$

$$c_p - c_v = \frac{\beta^2 T v}{K}$$

- Thus at any state defined by T and v, c_v can be found if c_p, β and K are known for the substance at that state. The values of T, v and K are always positive and, although β may sometimes be negative (e.g., between 0° and 4°C water contracts on heating at constant pressure), β^2 is always positive. It follows that c_p is always greater than c_v

$$Since, c_v = \left(\frac{\partial u}{\partial T} \right)_v = \left(\frac{\partial u}{\partial s} \right)_v \left(\frac{\partial s}{\partial T} \right)_v$$

$$we have, c_v = T \left(\frac{\partial s}{\partial T} \right)_v$$

$$similarly, c_p = \left(\frac{\partial h}{\partial T} \right)_p = \left(\frac{\partial h}{\partial s} \right)_p \left(\frac{\partial s}{\partial T} \right)_p$$

$$Hence, c_p = T \left(\frac{\partial s}{\partial T} \right)_p$$

Alternative Expressions for Internal Energy and Enthalpy

(i) Alternative expressions for equations can be obtained as follows :

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$$

$$But, \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)\left(\frac{\partial v}{\partial p}\right)_T = -1$$

$$or, \left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T = +\frac{\beta v}{kv} = \frac{\beta}{k}$$

$$soweet, \left(\frac{\partial u}{\partial v}\right)_T = T\frac{\beta}{k} - p$$

$$Thus, du = c_v dT + \left(\frac{T\beta}{k} - p\right)dv$$

$$similarly, \left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$$

$$Butbydefinition, \left(\frac{\partial u}{\partial T}\right)_p = \beta v$$

$$Hence, \left(\frac{\partial h}{\partial p}\right)_T = v(1 - \beta T)$$

$$Thus, dh = c_p dT + v(1 - \beta T)dp$$

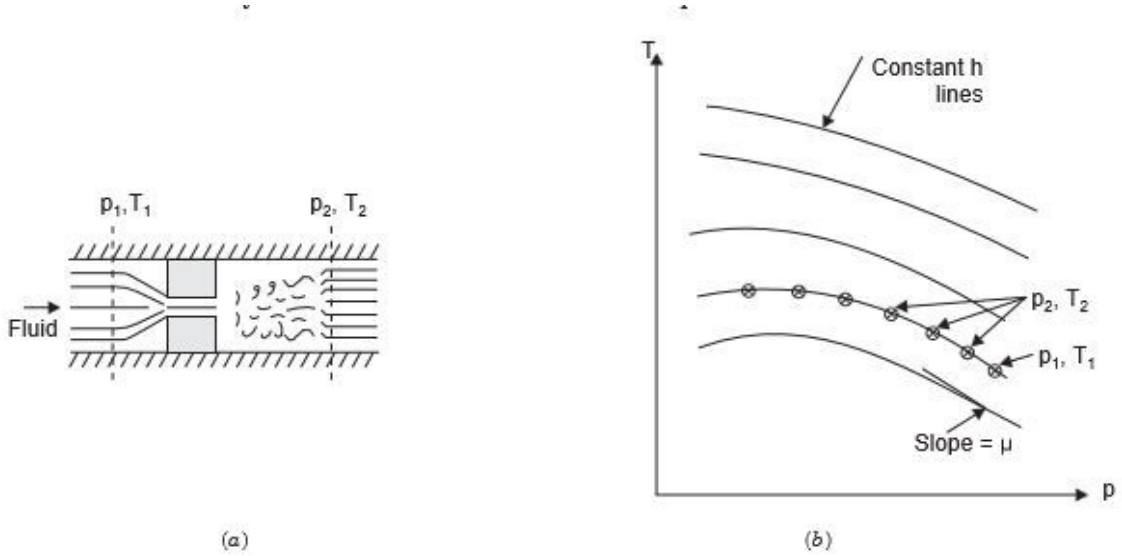
$$(ii) \sin ce, u = h - pv$$

$$or, \left(\frac{\partial u}{\partial p}\right)_T = \left(\frac{\partial h}{\partial p}\right)_T - p\left(\frac{\partial v}{\partial p}\right)_T - v = v - v\beta T + pkv - v$$

$$Hence, \left(\frac{\partial u}{\partial p}\right)_T = pkv - v\beta T$$

Joule-Thomson Co-efficient

- Let us consider the partial differential co-efficient $\left(\frac{\partial T}{\partial p}\right)_h$ We know that if a fluid is flowing through a pipe, and the pressure is reduced by a throttling process, the enthalpies on either side of the restriction may be equal.
- The throttling process is illustrated in Fig.(a). The velocity increases at the restriction, with a consequent decrease of enthalpy, but this increase of kinetic energy is dissipated by friction, as the eddies die down after restriction. The steady-flow energy equation implies that the enthalpy of the fluid is restored to its initial value if the flow is adiabatic and if the velocity before restriction is equal to that downstream of it. These conditions are very nearly satisfied in the following experiment which is usually referred to as the Joule-Thomson experiment.



- Through a porous plug (inserted in a pipe) a fluid is allowed to flow steadily from a high pressure to a low pressure. The pipe is well lagged so that any heat flow to or from the fluid is negligible when steady conditions have been reached. Furthermore, the velocity of the flow is kept low, and any difference between the kinetic energy upstream and downstream of the plug is negligible.
- A porous plug is used because the local increase of directional kinetic energy, caused by the restriction, is rapidly converted to random molecular energy by viscous friction in fine passages of the plug. Irregularities in the flow die out in a very short distance downstream of the plug, and temperature and pressure measurements taken there will be values for the fluid in a state of thermodynamic equilibrium.
- By keeping the upstream pressure and temperature constant at p_1 and T_1, the downstream pressure p_2 is reduced in steps and the corresponding temperature T_2 is measured. The fluid in the successive states

defined by the values of p_2 and T_2 must always have the same value of the enthalpy, namely the value of the enthalpy corresponding to the state defined by p_1 and T_1. From these results, points representing equilibrium states of the same enthalpy can be plotted on a T-s diagram, and joined up to form a curve of constant enthalpy. The curve does not represent the throttling process itself, which is irreversible. During the actual process, the fluid undergoes first a decrease and then an increase of enthalpy, and no single value of the specific enthalpy can be ascribed to all elements of the fluid. If the experiment is repeated with different values of p_1 and T_1, a family of curves may be obtained (covering a range of values of enthalpy) as shown in Fig (b).

- The slope of a curve [Fig. 7.3 (b)] at any point in the field is a function only of the state of the fluid, it is the Joule-Thomson co-efficient μ, defined by $\mu = \left(\frac{\partial T}{\partial p}\right)_h$

- The change of temperature due to a throttling process is small and, if the fluid is a gas, it may be an increase or decrease. At any particular pressure there is a temperature, the temperature of inversion, above which a gas can never be cooled by a throttling process.

- Both cp and μ, as it may be seen, are defined in terms of p, T and h. The third partial differential co-efficient based on these three properties is given as follows :

$$\left(\frac{\partial h}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_h \left(\frac{\partial T}{\partial h}\right)_p = -1$$

$$Hence, \left(\frac{\partial h}{\partial p}\right)_T = -\mu c_p$$

μ may be expressed in terms of c_p, p, v and T as follows :

The property relation for dh is dh = T ds + v dp

From second T ds equation, we have

$$Tds = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$$

$$\therefore dh = c_p dT - \left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]dp$$

$$For, cons\tan tenthalpyprocess, dh = 0, therefore$$

$$0 = (c_p dT)_h + \left[\left\{v - T\left(\frac{\partial v}{\partial T}\right)_p\right\}dp\right]_h$$

$$or, \left(c_p dT\right)_h = \left[\left\{T\left(\frac{\partial v}{\partial T}\right)_p - v\right\}dp\right]_h$$

$$\therefore \mu = \left(\frac{\partial T}{\partial p}\right)_h = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]$$

$$For anidea\lg as$$

$$pv = RT, v = \frac{RT}{p}$$

$$or, \left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} = \frac{v}{T}$$

$$\therefore \mu = \frac{1}{c_p}\left(Tx\frac{v}{T} - v\right) = 0$$

Therefore, if an ideal gas is throttled, there will not be any change in temperature.

Let h = f(p, T)

$$Then, dh = \left(\frac{\partial h}{\partial p}\right)_T dp + \left(\frac{\partial h}{\partial T}\right)_p dT$$

$$But, \left(\frac{\partial h}{\partial T}\right)_p = c_p$$

$$\therefore dh = \left(\frac{\partial h}{\partial p}\right)_T dp + c_p dT$$

$$For throttling process, dh = 0$$

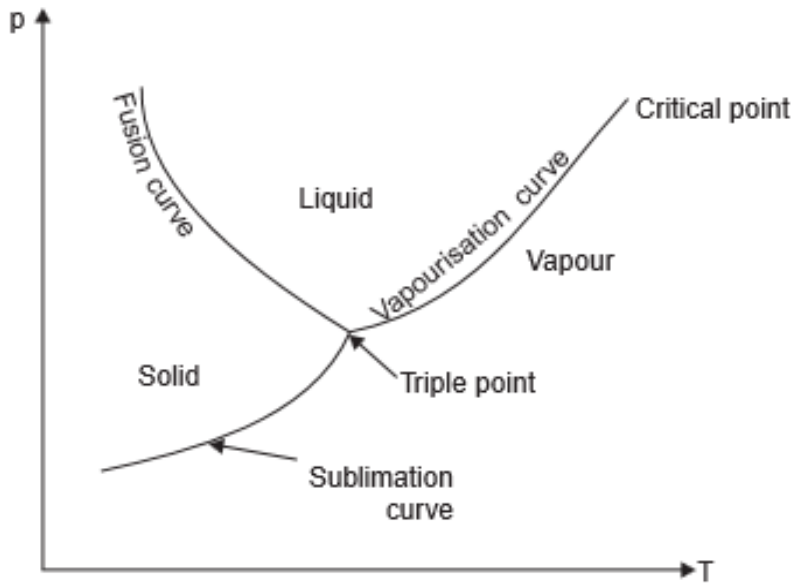
$$\therefore 0 = \left(\frac{\partial h}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_h + c_p$$

$$or, c_p = -\frac{1}{\mu}\left(\frac{\partial h}{\partial p}\right)_T$$

$\left(\frac{\partial h}{\partial p}\right)_T$, is known as the constant t emperature co - efficient

CLAUSIUS-CLAPERYON EQUATION

- Clausius-Claperyon equation is a relationship between the saturation pressure, temperature, the enthalpy of evaporation, and the specific volume of the two phases involved. This equation provides a basis for calculations of properties in a two-phase region. It gives the slope of a curve separating the two phases in the p-T diagram.



- The Clausius-Claperyon equation can be derived in different ways. The method given below involves the use of the Maxwell relation

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

- Let us consider the change of state from saturated liquid to saturated vapour of a pure substance which takes place at constant temperature. During the evaporation, the pressure and temperature are independent of volume.

$$\left(\frac{dp}{dT}\right) = \frac{s_g - s_f}{v_g - v_f}$$

where, s_g = Specific entropy of saturated vapour, s_f = Specific entropy of saturated liquid, v_g = Specific volume of saturated vapour, and v_f = Specific volume of saturated liquid.

$$Also, s_g - s_f = s_{fg} = \frac{h_{fg}}{T}$$

$$and, v_g - v_f = v_{fg}$$

where s_{fg} = Increase in specific entropy, v_{fg} = Increase in specific volume, and h_{fg} = Latent heat added during evaporation at saturation temperature T.

$$\left(\frac{dp}{dT}\right) = \frac{s_g - s_f}{v_g - v_f} = \frac{s_{fg}}{v_{fg}} = \frac{h_{fg}}{Tv_{fg}}$$

This is known as Clausius-Claperyon or Claperyon equation for evaporation of liquids.

The derivative dp /dT is the slope of vapour pressure versus temperature curve. Knowing this slope and the specific volume vg and vf from experimental data, we can determine the enthalpy of evaporation, ($h_g - h_f$) which is relatively difficult to measure accurately.

Clausius-Claperyon or Claperyon equation is also valid for the change from a solid to liquid, and from solid to a vapour. At very low pressures, if we assume $v_g = v_{fg}$ and the equation of the vapour is taken as pv = RT, then eqn. becomes

$$\frac{dp}{dT} = \frac{h_{fg}}{Tv_g} = \frac{h_{fg}\,p}{RT^2}$$

$$or, h_{fg} = \frac{RT^2}{p}\frac{dp}{dT}$$

Eqn. above may be used to obtain the enthalpy of vapourisation. This equation can be rearranged as follows :

$$\frac{dp}{p} = \frac{h_{fg}}{R}\frac{dT}{T^2}$$

Integratin g the above equation, we get

$$\int \frac{dp}{p} = \frac{h_{fg}}{R}\int \frac{dT}{T^2}$$

$$\ln \frac{p_2}{p_1} = \frac{h_{fg}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

- Knowing the vapour pressure p1 at temperature T_1 we can find the vapour pressure p_2 corresponding to temperature T_2 from above eqn.
- we see that the slope of the vapour pressure curve is always +ve, since $v_g > v_f$ and h_{fg} is always +ve. Consequently, the vapour pressure of any simple compressible substance increases with temperature. — It can be shown that the slope of the sublimation curve is also +ve for any pure substance. — However, the slope of the melting curve could be +ve or –ve. — For a substance that contracts on freezing, such as water, the slope of the melting curve will be negative.